Transactions of the Materials Research Society of Japan 26 [4] 1151-1153 (2001)

Effect of Hydrostatic Pressure on Single Wall Carbon Nanotube Bundles

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(10,10) type single wall carbon nanotube bundles are shown to undergo a structural phase transformation from an approximately hexagonal (actually monoclinic) to a monoclinic structure at a pressure of about 1.3 GPa in good agreement with recent experimental evidence. Hysteresis and discontinuity in the lattice parameters indicates that this reversible transformation is of the first order.

Key words: nanotubes, phase transformation, hydrostatic pressure, SWCNT bundles

1. INTRODUCTION

Recently, the behavior of single wall carbon nanotube bundles (SWCNT) has gained considerable attention [1,2,3]. Although it appears well established that a phase transformation occurs at a hydrostatic pressure of about 1.5 to 1.7 GPa, the nature of this transformation is not yet clear.

Venkateswaran et al. [1] determined a transformation at 1.5 GPa by the disappearance of Raman modes associated with the radial breathing mode of nanotubes. They attribute this to a hexagonal distortion of the initially cylindrical nanotubes at increased pressure. Peters et al. [2] determined a transformation at 1.7 GPa using the same technique but interpreted their results on the basis of empirical force field calculations as a structural phase transformation in which the nanotubes take an oval cross section and the lattice distorts from monoclinic to triclinic. Finally Tang et al. [3] using synchrotron X-ray diffraction found that the nanotubes undergo polygonization while the hexagonal lattice remains intact, thereby concluding with reference [1].

To shed light on these contradictory finding we performed *ab initio* simulations on (10,10) SWCNT as a function of pressure. (10,10) SWCNT are of the armchair type and are semiconducting. Ultrasoft pseudopotentials [4] were used with a plane wave basis with a cutoff energy of 360 eV, the exchange correlation potential was of the generalized gradient approximation type [5]. Calculations were performed with a single nanotube per unit cell, amounting to 40 atoms per cell. Reciprocal space integrations were carried out with the Monkhorst-Pack "special k-points" method [6] using 7x1x1 kpoints. Structural optimizations were carried out with high precision with as convergence criterion that the force on each atom was less than 1 meV/bohr.

2. RESULTS AND DISCUSSION

We considered two cases, imposing hexagonal symmetry for the unit cell, and without imposing hexagonal symmetry for the unit cell. We found that releasing the hexagonal symmetry constraint always lowered the enthalpy. However, it should be mentioned that when hexagonal symmetry was imposed no abrupt phase transformation occurred in the 0 to 2 GPa pressure range, but instead only a gradual polygonization of the nanotubes was observed as reported earlier by Venkateswaran et al. [1] and Tang et al. [3].

When no symmetry constraints were imposed we obtained a monoclinic (nearly hexagonal) to monoclinic phasetransformation where the SWCNTs adopted an oval cross section simultaneously, as reported earlier by Peters et al [2].

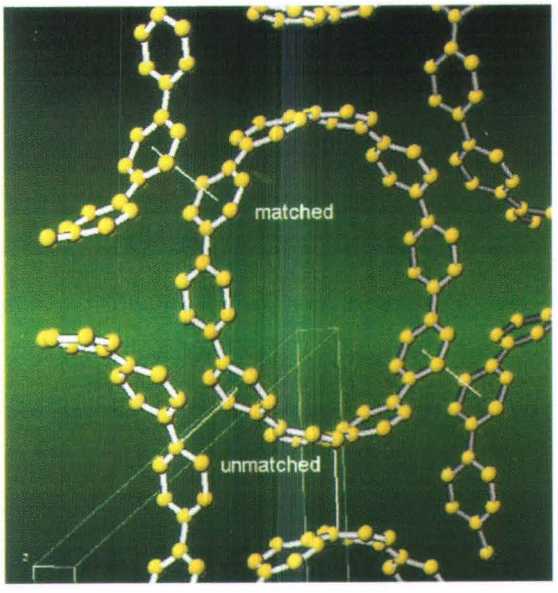

Fig. 1 (10,10) single wall carbon nanotubes are not commensurate with hexagonal symmetry. "matched" indicates a hexagon center to hexagon center alignment, and "unmatched" indicates a hexagon center to hexagon corner alignment.

It is important to point out that even at zero pressure the SWCNT bundles are not hexagonal because the (10,10) nanotubes are commensurate with neither 6-fold, nor with 3-fold symmetry. Fig. 1 illustrates that four neighbors of a nanotube have the preferred "hexagon center" to "hexagon corner" alignment, while two neighbors have the less favorable "hexagon center" to "hexagon center" alignment. As a consequence the lattice is not hexagonal but monoclinic because the translation vectors perpendicular to the length of the

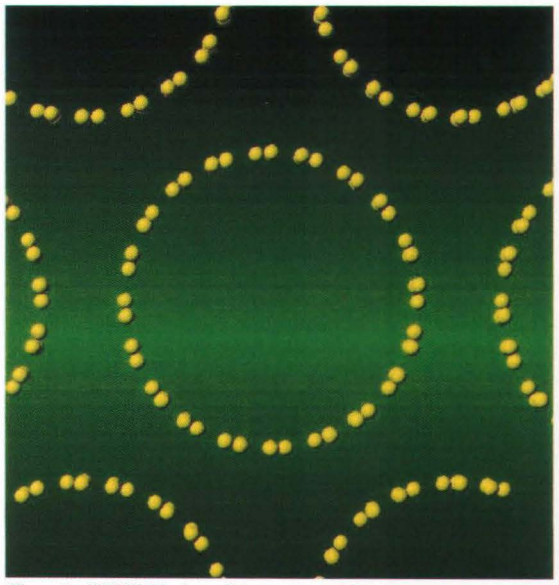

Fig. 2 SWCNT bundle at zero hydrostatic pressure, initial structurally optimized configuration.

SWCNT are of unequal length.

Our calculations started at a zero initial hydrostatic pressure and the pressure was increased in steps of 0.5 GPa. At zero pressure the intertube distances were 3.94 and 4.02 Angstrom and the SWCNT were cylindrical, see Fig. 2. At 2.5 GPa the structure appeared little changed except for a reduction in the intertube distance to 3.10 and 3.32 Angstrom, see Fig. 3. It should be noted that the angle between the translation vectors perpendicular to the length of the SWCNT remained about 60 degrees.

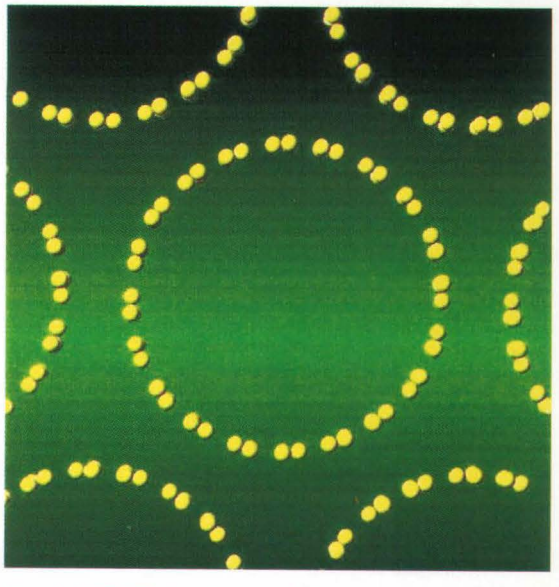

Fig. 3 SWCNT bundle at 2.5 GPa hydrostatic pressure. Pressure was gradually increased from 0 GPa.

The calculation that followed, at 3.0 GPa, revealed the transformed structure, the angle is reduced to 50.85 degrees, making for a monoclinic structure, moreover the SWCNTs have become oval and the translation vectors have become much more unalike in length. The intertube distances are now 2.90 and 3.10 Angstrom, see Fig. 4.

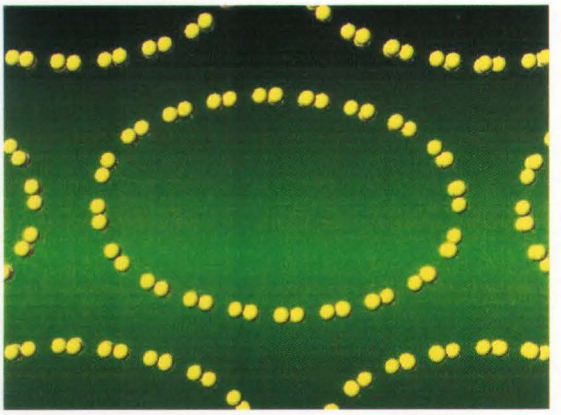

Fig. 4 SWCNT bundle at 3.0 GPa hydrostatic pressure. Pressure was gradually increased from 0 GPa.

Next, the pressure is reduced in steps of 0.1 GPa. At 1.4 GPa the structure still has not returned to the original nearly hexagonal type but the intertube distance has increased again to 3.22 and 3.24 Angstrom and the angle has increased to 55 degrees, see Fig. 5.

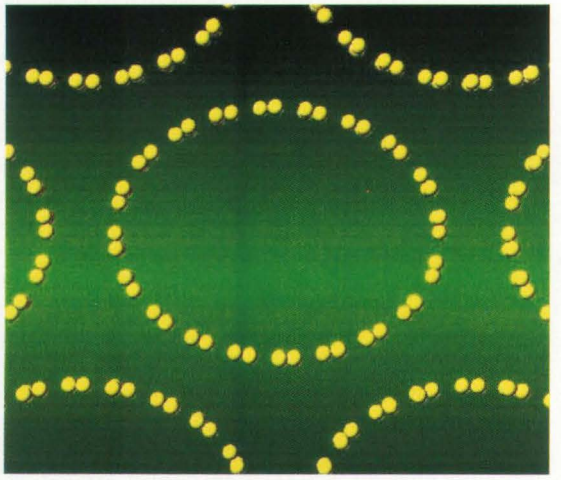

Fig. 5 SWCNT bundle at 1.4 GPa hydrostatic pressure. Pressure was gradually decreased from 3.0 GPa.

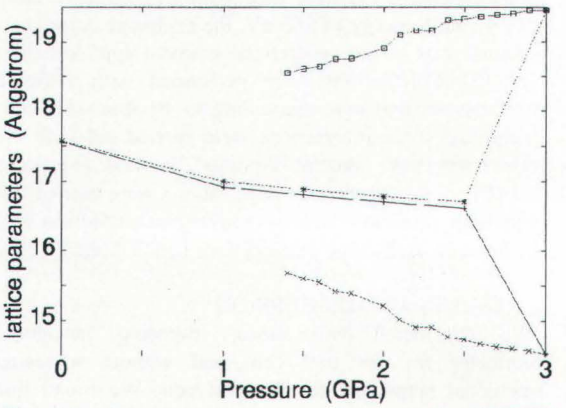

Fig. 6 Lattice parameters perpendicular to the SWCNT as a function of hydrostatic pressure. Notice the phase transformation that occurs upon increasing the pressure from 2.5 to 3.0 GPa.

The hysteresis is indicative of a first order phase transformation. The lattice parameters as a function of pressure also illustrates the discontinuous nature of the transformation, see Fig. 6.

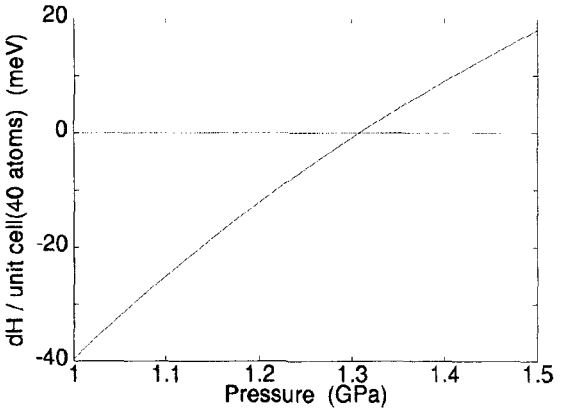

Fig. 7 Enthalpy of nearly hexagonal phase minus enthalpy of monoclinic phase as a function of pressure. Note that the two phases are at equilibrium at a hydrostatic pressure of 1.3 GPa

A careful examination of the enthalpy difference between the nearly hexagonal and monoclinic phases reveals that the two phases are at equilibrium at a hydrostatic pressure of 1.3 GPa, see Fig. 7.

It is possible that in SWCNT bundles consisting of nanotubes that are commensurate with hexagonal symmetry a completely different behavior under hydrostatic pressure occurs. In such bundles there is no build-in monoclinic distortion that predisposes the nanotubes to transform from a round to an oval cross section. It is possible that in such nanotubes the polygonization as reported by Venkateswaran et al. [1] and Tang et al. [3] occurs. Therefore, we are currently calculating the behavior of (12,12) and (18,0) SWCNT bundles, which have perfect hexagonal structures at zero pressure, under hydrostatic pressure.

3. CONCLUSION

The nature of the phase transformation in single wall carbon nanotube bundles under hydrostatic pressure has been identified as a first order monoclinic (nearly hexagonal) to monoclinic structural phase transformation for the case of (10,10) armchair type nanotubes. The computed transition pressure of 1.3 GPa is in fair agreement with experimentally determined pressure of 1.5 to 1.7 GPa. In nanotubes that are commensurate with the hexagonal lattice qualitatively different behavior may occur. This would explain the contradictory reports in the literature concerning the behavior at hydrostatic pressure. Current calculations on (12,12) armchair and (18,0) zigzag type nanotubes may bear this out.

4. REFERENCES

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(Received December 8, 2000; Accepted February 8, 2001)